Colloidal Electrolytes.—Soap Solutions and their Constitution.[*]

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I. *Introduction.*

Colloidal electrolytes are solutions of salts in which one ion has been replaced by a heavily hydrated polyvalent micelle, carrying an equivalent sum total of electrical charges and also serving as an excellent conductor of electricity. This is the conclusion to which our investigations have led us.

It will probably prove that this new class includes, under certain conditions, most organic compounds containing more than eight carbon atoms, and capable of forming ions, also solutions of the acid and alkali proteins, dyes, indicators, sulphonates, soaps, and possibly even of such compounds as chromium chloride, and of the alkaline tungstates, zincates, tellurates, and silicates. Many non-aqueous solutions may also be included in the same category, as will be shown in a later communication, and it is indeed probable that the class includes as many members as the acids and bases together.

II. *Résumé of previous Work.*

In 1905 one of us had shown that the available data with regard to solutions of such substances as cadmium iodide could be readily interpreted by means of the theory of ionic dissociation (without modifying it). In 1908 the investigation of solutions of salts, possessing simple formulæ, but exhibiting apparently abnormal properties, was extended to include the alkaline salts of the normal saturated fatty acids. In planning the investigation it was decided to adopt only such methods as had been employed in establishing the theories of solutions and of electrolytes, such as the measurement of freezing-points, of vapour-pressures, of electrical conductivities, etc. Viscosity measurements, and other methods employed in the investigation of colloids, were regarded as furnishing evidence of a circumstantial character only.

The first part of the investigation consisted in measuring the conductivities of solutions of sodium palmitate, over a wide range of concentration, near the boiling-point, at which alone they were liquid. The apparent boiling-points of numerous soap solutions had been measured by Krafft, but, as is shown in the present communication, the results arrived at, which had been accepted as a proof that soap was a simple colloid, were entirely erroneous.

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[*] Abridged manuscript.

The conductivity measurements proved conclusively that soap solutions possessed a high conductivity, not only when dilute, as had been shown by Kahlenburg and Schreiner, but even in the highest concentrations, indicating that soap solutions must consist of something other than neutral colloid. The next step was to show by two independent methods, namely, measurements of the rate of catalysis and of electromotive force, that the concentration of the hydroxyl ion in the solutions was negligible. *Hence the high conductivity must be due to the soap itself.*

III. *The Experimental Method.*

One of us, in conjunction with Miss Taylor, has already proved that neither the direct boiling-point method nor the tensimeter method can be used in the measurement of the vapour-pressures of soap solutions, owing to the impossibility of eliminating the errors due to the presence of air. For this reason, Krafft's observation that soap solutions boil at a temperature just above or just below the boiling-point of water, although perfectly correct, is entirely without significance. In the present investigation, therefore, the rise of boiling-point or lowering of the vapour-pressures of the solutions was measured by a modification of Cumming's *dew-point* method, in which the results are not influenced by the presence of air in the apparatus. This method made it possible to cover a wide range of concentration, from dilute solutions up to almost anhydrous solids. Independent measurements of a number of the solutions were made by each of us separately, and on subsequent comparison the maximum difference between our observations amounts to 0·01°.

Fig. 1 shows a diagram in vertical section of the apparatus employed. A highly polished silver tube, *a*, with silver bottom, is closed with a rubber stopper at the top. Through the stopper are inserted a thermometer and two tubes, through which a rapid current of water is circulated by a power pump from and to a thermostat of adjustable temperature. The silver tube is held in a cork in a glass vessel, which contains the solution to be studied. The top of the glass vessel rises an inch or so above the cork, so that the closed space is completely immersed in the water of a thermostat, which has glass slides. A capillary glass tube, sealed to a stopcock, passes through the cork holding the silver tube, and may be connected with a water pump and thus evacuated, or the pressure adjusted to any desired value.

The following procedure alone rendered possible the attainment of accurate results. Even if the silver tube is kept highly polished, it is extremely difficult to detect the first very slight dimming of the silver surface. This difficulty may, however, be overcome by treating a definite portion of the silver surface so that no dew deposits on it, and it therefore remains bright, directly contrasting with the slightly clouded surface adjacent to it. The test of the appearance, or disappearance, of dew is then by the first appearance of this sharp boundary or by the perfect uniformity of the surface. To produce this effect, boiling water is run through the silver tube, and the bottom angle at one side of the tube is dipped once into boiling conductivity water. The water evaporates at once, but thereafter no dew will form on that part of the surface which has been treated. When the tube is subsequently viewed from the front a boundary line runs diagonally across the lowest part of the side of the tube. An attempt was made to extend this refinement of the dew point method to various non-aqueous solutions, but without success, for in every case dew formed all over the silver surface.

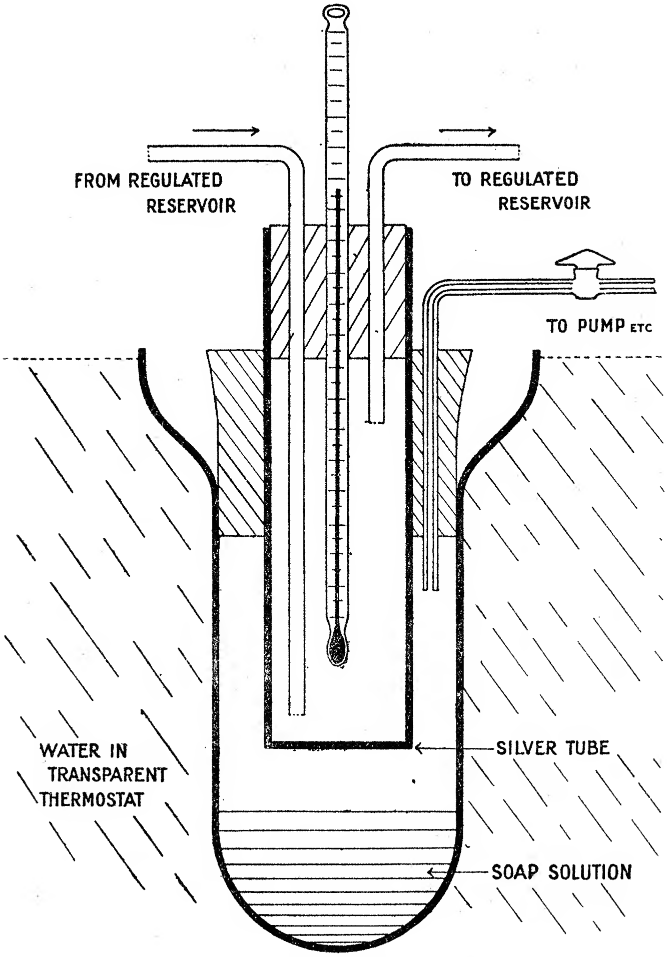

Fig. 1.—Section of Dew Point Apparatus.

The transparent thermostat was connected with a constant level device and was filled with glycerine and water, the top being carefully covered to reduce evaporation. The liquid was stirred vigorously during an experiment. The sides of the thermostat were cleaned and polished. The auxiliary thermostat contained water under a layer of melted paraffin or was covered. It was heated by gas, controlled by screw-down valve with a divided head, so that the rate of heating could be rapidly and accurately adjusted.

In making an experiment, the temperature of the transparent thermostat was first adjusted, generally to 90°. Water, very near its boiling-point, was then circulated through the silver tube, which was inserted in the glass tube, so that the bottom of it was 1 cm. above the surface of the solution to be studied. The whole apparatus was then placed in the transparent thermostat, and so held that it was possible to shake it slightly, so as to renew the surface of the solution from time to time. After a few minutes, the stopcock sealed to the capillary tube was closed, but it was not found necessary to evacuate the air from the apparatus, as the small amount of air present caused no appreciable lag in the diffusion of the water vapour.

The temperature of the water running through the silver tube was now very gradually lowered, and on the first appearance of dew, shown by a slight discontinuity in the polished silver surface, the boundary line becoming faintly visible under bright and carefully adjusted illumination, both thermometers were read. The rate of the supply of heat to the auxiliary thermostat was then at once increased to a value which would cause the temperature of the running water to rise slowly. Though the dew at first increased, it soon became faint, and suddenly disappeared, the silver surface becoming sensibly uniform. The two thermometers were now read a second time. The temperature of the auxiliary thermostat was then again raised, and the whole cycle of operations repeated several times, so as to obtain a series of readings of the two thermometers at the points at which the dew formed and disappeared. The mean values for two series of seven or eight readings in either direction by independent observers show a negligible difference.

The results of a series of experiments are set down in Table I.

Measurements with two completely independent solutions on different occasions and involving eighteen readings gave as result 0·20° and 0·205°.

The difference between the temperature at which the dew forms and disappears is due to the alternate concentration and dilution of the surface layers of the soap solution, but it is probable that the error is equally distributed between the two sets of results, and that the mean of the two series gives the true dew point. In subsequent experiments, in which the solution was stirred, the difference practically disappeared. In determining the dew point with pure water, in order to arrive at the thermometer error and to eliminate personal error of observation, it was found that the difference never exceeded 0·03°.

Table I.—Dew Point of 1·0 N. Potassium Stearate at 90°.

Silver tube thermometer.	Thermostat thermometer.	Temperature difference.	
		Formation.	Disappearance.
89·43	90·00	(0·57)	
89·75	90·01		0·26
89·68	90·01	0·33	
89·75	90·00		0·25
89·68	90·00	0·32	
89·74	90·01		0·27
89·68	90·00	0·32	
89·75	90·01		0·26
89·69	90·00	0·31	
89·74	90·00		0·26
Mean		0·32	0·26
Final mean		−0·29°	
Thermometer error		−0·09°	
Rise of boiling point due to soap		0·20° at 90° C.	

IV. *The Method of Calculation.*

At the apparent dew point we have pure water, deposited on the silver tube, in equilibrium with its vapour, which is also in equilibrium with the soap solution, at a slightly higher temperature. The pressure of the aqueous vapour can be obtained by reference to standard tables, and the difference between the temperatures of the pure water and the soap solutions, as determined by the readings of the thermometers in the silver tube and in the transparent thermostat, corresponds to the rise of boiling-point of the solution, at that pressure, due to the presence of the soap. According to the familiar van't Hoff formula, $\Delta t = RT^2/\lambda$, the rise in boiling-point for a 1·0 N solution of crystalloid, such as sugar, at 90°, should be 0·483°, a value which is slightly lower than the value at 100°, as T is greater and λ is less at the higher than at the lower temperature. In calculating the results of measurements by the well-known Beckmann method at 100°, the rise of boiling-point is assumed to be 0·510°.

For lower temperatures, the values of the constant are: 70°, 0·414°; 45°, 0·353°; 25°, 0·303°; 20°, 0·291°.

The results calculated by the related formula, $ln(p/p') = n/N$, give practically identical results, and it is worth emphasising the fact that these simple formulæ are still approximately correct even at high concentrations, the calculated osmotic effect always being higher than would have been anticipated. This is generally accounted for by assuming that the solute is hydrated. In a 2·7 N solution of cane-sugar, containing approximately equal weights of the constituents, the deviation is less than 12 per cent., and the hydrate appears to contain five molecules of water to one molecule of sugar.* These points have a certain bearing upon the results of the present investigation.

V. *The Experimental Results of the Dew Point Method.*

The solutions were prepared in silver tubes from Kahlbaum's best chemicals, employing all the precautions described in previous communications. The weight of palmitic acid required to neutralise a known amount of sodium hydroxide in aqueous alcohol was only 0·1 per cent. smaller than the theoretical amount.

Each concentration up to 1·5 N was prepared separately, and at least in duplicate. Concentrations are expressed invariably in weight normality (number of gram equivalent weights of soap in 1000 grams of water).

Almost every number in Table II and Table III is the resulting mean of several series of measurements, such as are given in Table I, carried out on independent solutions.

Table II.—Rise of Boiling Point at 90° for Potassium Salts.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Decoate caprate, C_{10}.	Octoate caprylate, C_8.	Hexoate caproate, C_6.	Acetate, C_2.
0·2 N	0°·10	0°·12	0°·13	0°·15	0°·16	0°·17	0°·17	0°·185
0·5 N	0·17	0·19	0·23	0·26	0·31	0·35	0·38	0·46
0·75 N	0·19	0·23	0·27	0·30	0·42	0·48	0·53	
1·0 N	0·20	0·24	0·28	0·32	0·52	0·60	0·66	0·86
1·5 N	0·16	0·21	0·25	0·31	(0·65)			
2·0 N	0·18	0·27	0·32	0·48	(0·72)	0·79		
3·0 N	0·23	—	—	1·02				

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* 'Trans. Faraday Soc.,' vol. 11, p. 39 (1915).

Table III.—Rise of Boiling Point at 90° for Sodium Salts.

Weight normality.	Behenate, C_{22}.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprylate, C_8.	Acetate. C_2.	Any non-electrolyte by theory.
0·2 N	0°·09	0°·11	0°·13	0°·14	0°·15	0°·17	—	0°·10
0·5 N	0·11	0·18	0·20	0·24	0·28	0·37	0·45	0·24
0·75 N	—	0·22	0·24	0·28	0·32	0·50	—	0·38
1·0 N	0·09	0·23	0·25	0·29	0·34	0·62	0·84	0·48
1·5 N	—	0·18	0·22	0·27	0·33	—	—	0·72
2·0 N	0·11	0·19	0·50	—	—	—	1·38	0·97
3·0 N	—	0·30	1·23	—	—	—	2·32	1·45

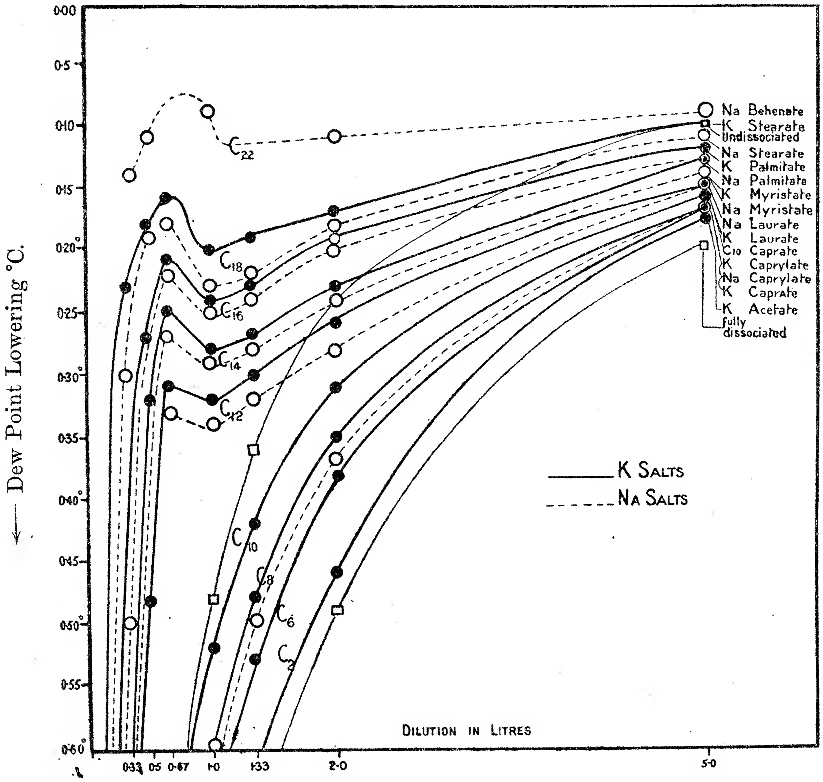

Fig. 2.—Dew Point Lowerings at 90° C. caused by Potassium and Sodium Salts of Fatty Acids.

Fig. 2 presents the directly observed dew point lowerings plotted against the dilution in litres as abscissæ. The curves for the sodium soaps are dotted in for convenience of comparison. It is evident that the salts fall into two classes. From the acetate up to the caprate (C_{10}) the curves are regular showing dissociation, although in the more concentrated caprate solutions the lowering only slightly exceeds that of an ordinary non-electrolyte. On the other hand, from the laurate (C_{12}) upwards, each curve passes through a pronounced maximum lowering at about 1·0 normal,* and a definite minimum lowering again at 1·5 normal. Above these concentrations the lowering rapidly increases again.

It is worth while remembering the physical properties of the solutions in question while discussing the regularity of the results. 1·5 N sodium stearate at 90° is a viscid gum. On the other hand, 2·0 N potassium laurate solution, with a similarly shaped curve, is a clear, oily liquid. The form of the curve is thus definitely due to the constituents in solution, not to mechanical effects, such as formation of gel or change of state. The effect is also not due to hysteresis, as is the case in the dehydration of certain gels, for it is independent of the age or method of preparation of soap solution, or whether water may have been previously added or taken away.

VI. *The Crystalloidal Constituents of Soap Solutions.*

Tables IV and V give the total concentrations of crystalloidal matter indicated by the data of Tables II and III, as shown in Section V above, and

Table IV.—Total Crystalloidal Matter in Potassium Salt Solutions at 90°.

Weight normality,	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate, C_{10}.	Caprylate, C_8.	Caproate, C_6.	Acetate, C_2.
0·2 N	0·21	0·25	0. 27	0·31	0·33	0·35	0·35	0·38
0·5 N	0·35	0·39	0·48	0·54	0·64	0·72	0·79	0·95
0·75 N	0·39	0·48	0·56	0·62	0·87	0·99	1·10	
1·0 N	0·42	0·50	0·58	0·66	1·08	1·24	1·37	1·78
1·5 N	0·33	0·44	0·52	0·64	1·35			
2·0 N	0·37	0·56	0·66	0·99	1·50	1·64		
3·0 N	0·48	—	—	2·11				

Table V.—Total Crystalloidal Matter in Sodium Salt Solutions at 90°.

Weight normality.	Behenate, C_{22}.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprylate, C_8.	Acetate, C_2.
0·2 N	0·19	0·23	0·27	0·29	0·33	0·35	
0·5 N	0·23	0·37	0·41	0·50	0·58	0·77	0·93
0·75 N	—	0·46	0·50	0·58	0·66	1·04	
1·0 N	0·19	0·48	0·52	0·60	0·70	1·28	1·74
1·5 N	—	0·37	0·46	0·56	0·68		
2·0 N	0·23	0·39	1·04	—	—	—	2·86
3·0 N	—	0·62	2·55	—	—	—	4·80

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* The exact concentration is slightly higher than 1·0 N for the lower members, and slightly lower than 1·0 N for the behenate. This agrees with the previous work on conductivity published from this laboratory, 'Trans. Chem. Soc.,' vol. 105, p. 435 (1914).

expressed in mols per 1000 grammes of water. This crystalloidal matter comprises K and Na; simple fatty acid ion, such as palmitate ion P; and simple undissociated neutral soap, such as sodium palmitate, NaP.

In fig. 3 the values of van't Hoff's factor "*i*," the ratio of the observed values of the lowering of the vapour pressures to the predicted values for solutions of any non-electrolyte of the same concentration, are plotted against the values of the dilution. The curves express the proportion of total crystalloids present, relative to that in the case of a non-electrolyte which is taken as unity, that of a completely dissociated binary electrolyte being 2.

It will be noted that the standpoint taken up differs from the crude treatment almost invariably accorded to measurements of "molecular weight" by the methods of ebullioscopy and cryoscopy, whether in aqueous or non-aqueous solution, where the data are simply scanned for evidence of association or dissociation. The usual interpretation is to conclude that, for example, a N/5 potassium stearate or a N/2 sodium myristate consists of simple undissociated molecules (a result which is, of course, irreconcilable with the conductivity, as in the case of many non-aqueous solutions). Similarly, a normal solution of sodium or potassium palmitate would be regarded as being composed of undissociated double molecules (again irreconcilable with the high conductivity). It will be seen how the method, developed under headings VI and VII, will probably clear up many otherwise unexplained anomalies in non-aqueous solutions, where such cases constantly occur.

The results cover a very wide range, from the ordinary highly dissociated electrolytes represented by the acetates to the concentrated solutions of the behenate (C_{22}), where the total amount of crystalloid, ionised and not, is only a tenth of the total concentration.

The regularity with which the phenomena set in is very striking, as we ascend the homologous series. The transition from any one type to the other is quite gradual. Again, the curves for each fatty acid run in pairs for the sodium and potassium salts. Only in concentrations above 1·5 N do the potassium and sodium soaps diverge appreciably, although in every case the potassium salt solution contains slightly more colloid. The last result had been already deduced from our study of conductivity.

VII. *The Combination of Osmotic with Conductivity Data.*

We have now the data derived from the experiments on vapour-pressure in suitable form to connect them with the data derived from conductivity experiments, with which they are at first sight at variance. The conductivity data which follow are based upon the values taken for the mobilities of the negative radicals at 90°: behenate to laurate 90, caprate 92, caprylate 94,

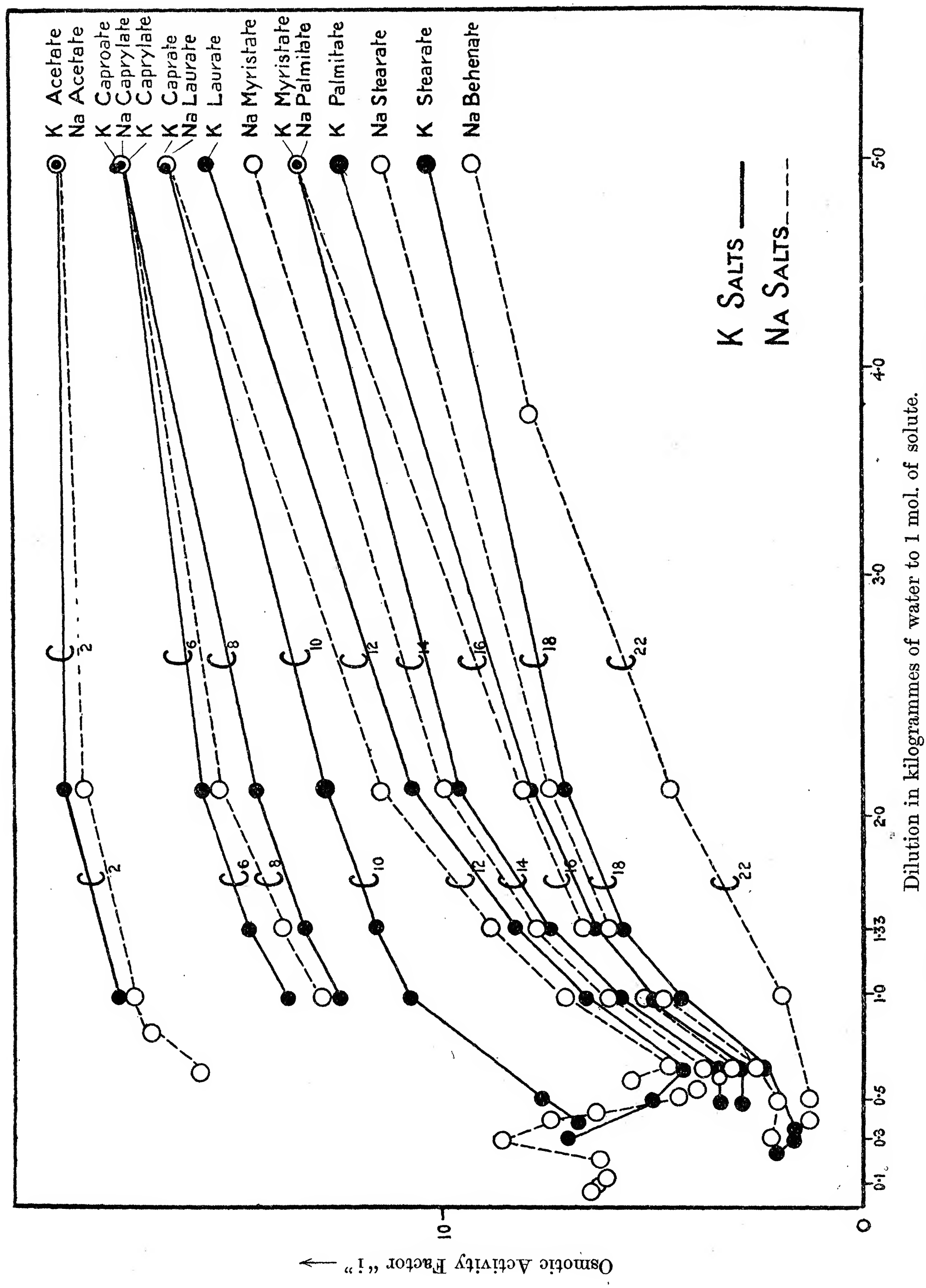

Fig. 3.—Relative Osmotic Activity. (10 in vertical scale should read 1·0.)

caproate 98, acetate 116, also sodium 139 and potassium 188. These are based partly upon the previous work,* partly on the measurements by A. A. Noyes and his co-workers at 100° for potassium and sodium chloride and acetate, and upon the extensive information which is available with regard to dependence of mobility upon molecular weight and chemical constitution in the case of organic anions. Direct determinations were being carried out in the early summer of 1914, and the experiments are now being completed. The values taken here must be substantially correct for the true ions, but, as we shall see in Section XI below, a still higher mobility must be ascribed to the ionic micelle. The concentrations of potassium or sodium ions thus deduced from the conductivity measurements are given in Tables VI and VII.

Table VI.—Concentration of Potassium Ions in Salts at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate, C_{10}.	Caprylate, C_8.	Caproate, C_6.	Acetate, C_2.
0·2 N	0·072	0·080	0·094	0·103	0·135	0·135	0·140	0·145
0·5 N	0·205	0·202	0·243	0·262	0·278	0·298	0·310	0·324
0·75 N	0·305	0·345	0·366	0·384	0·399	0·389	0·426	0·454
1·0 N	0·408	0·446	0·489	0·515	0·521	0·527	0·523	0·582
1·5 N	—	—	—	0·696	—	0·728	—	0·800
2·0 N	—	—	—	0·885	—	0·898	—	1·01

Table VII.—Concentration of Sodium Ions in Salts at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Acetate, C_2.
0·2 N	0·053	0·079	0·085	0·099	0·140
0·5 N	0·166	0·195	0·216	0·239	0·303
0·75 N	0·272	0·286	0·324	0·350	0·409
1·0 N	0·386	0·369	0·405	0·455	0·511
1·5 N	0·533	0·553	0·543	0·615	0·664

By subtracting the values in Tables VI and VII from those in Tables IV and V we arrive at Tables VIII and IX, which give the concentrations of all the crystalloidal constituents other than potassium or sodium ions. The remainder of the soap must of course be colloid, and the values for this are given in Tables X and XI.

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* 'Trans: Chem. Soc.,' vol. 105, p. 435 (1914).

Table VIII.—Concentration of Crystalloidal Constituents other than K at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate. C_{10}.	Caprylate, C_8.	Caproate, C_6.	Acetate, C_2.
0·2 N	0·14	0·17	0·18	0·21	0·20	0·22	0·21	0·24
0·5 N	0·15	0·19	0·23	0·28	0·36	0·43	0·43	0·63
0·75 N	0·08	0·11	0·19	0·24	0·47	0·58	0·67	
1·0 N	0·01	0·05	0·09	0·15	0·56	0·72	0·85	1·20
1·5 N	—	—	—	0·05				
2·0 N	—	—	—	0·11	—	0·74		

Table IX.—Concentration of Crystalloidal Constituents other than Na at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Acetate, C_2.
0·2 N	0·18	0·19	0·20	0·23	
0·5 N	0·20	0·22	0·28	0·34	0·63
0·75 N	0·18	0·21	0·26	0·31	
1·0 N	0·09	0·15	0·20	0·25	1·23
1·5 N	−0·20	−0·11	0·02	0·07	

Table X.—Concentration of Total Colloid in Potassium Salt Solution at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate, C_{10}.	Caprylate, C_8.	Caproate, C_6.	Acetate, C_2.
0·2 N	0·06	0·03	0·02	−0·01	0·00	−0·02	−0·01	−0·04
0·5 N	0·35	0·31	0·27	+0·22	0·14	+0·07	+0·02	−0·13
0·75 N	0·69	0·64	0·56	0·51	0·28	0·17	0·08	
1·0 N	0·99	0·95	0·91	0·85	0·44	0·28	0·15	−0·20
1·5 N	—	—	—	1·55				
2·0 N	—	—	—	1·89	—	1·26		

Table XI.—Concentration of Total Colloid in Sodium Salt Solutions at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Acetate, C_2.
0·2 N	0·02	0·01	0·00	−0·03	
0·5 N	0·30	0·28	0·22	+0·16	−0·13
0·75 N	0·57	0·54	0·49	0·44	
1·0 N	0·91	0·85	0·80	0·75	−0·23
1·5 N	(1·70)	1·61	1·48	1·43	

The first point to notice is that every 1·0 N solution, from the caproate (C_6) upwards, contains colloid. In the case of the caproate only 15 per cent. of the soap is present in this form, while in the potassium stearate solution 99 per cent. is colloid. This is in accordance with the results of former work from this laboratory on the appearance, washing power, density, and conductivity of soap solutions. The great increase in amount of colloid takes place in passing from the caprate (C_{10}) to the laurate (C_{12}), when it about doubles.

Again, in every case the amount of colloid falls off steadily and very rapidly with decrease of concentration. It appears to become inappreciable as measured at N/5 laurate; but an error of 0·01° in the dew point is equal to 10 per cent. in the concentration in this dilute solution, and it is probable that a small amount of colloid is still present.

It is necessary to consider the validity of this comparison of osmotic with conductivity data. It is undoubtedly the case that the osmotic values are too high, presumably, as already mentioned, on account of hydration of the solute (see Section IV above). The ebullioscopic method shows this particularly, for Beckmann, by this method, obtained values corresponding to dissociations which, in the case of sodium acetate, actually increased from 78 per cent. in N/4 solution to 95 per cent. in 1·9 N solution. The apparent dissociations of potassium and sodium chlorides pass through minima of 76 and 84 per cent. at about N/10, rising to 89 per cent. for 2·5 N KCl, and to the impossible value of 106 per cent. for 2·1 N NaCl.

The dew-point method is more reliable than the ebullioscopic method, since the latter measures only a very rough dynamic thermal equilibrium instead of a true static one. But even so, the dissociation for sodium acetate deduced from the conductivity falls short of the osmotic activity by 20 to 23 per cent. Were this deviation entirely due to hydration, seven or eight molecules of water would have combined with the acetate and its ions, a not improbable result in the light of other evidence.

On the other hand, the results of conductivity measurements are definitely too low, on account of the retarding influences of viscosity on the mobility of ions.

VIII. *The Evidence for the Existence of the Ionic Micelle.*

For convenience we shall discuss one particular example first, taking for this purpose the 1·0 N potassium stearate solution measured in Table I above. This solution has at that temperature of 90° an equivalent conductivity of 113·4 reciprocal ohms,* that of 1·0 N potassium acetate being 176·9 at the same temperature. It is evident that in this concentration the stearate conducts about two-thirds as well as the acetate itself, and that it must be recognised as an excellent conductor. Further, the concentration of free hydroxyl ion is only 0·002 N, which is quite negligible for our present purpose.

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* 'Trans. Chem. Soc.,' vol. 105, p. 424 (1914).

Taking the conductivity of potassium stearate for complete dissociation as $188 + 90 = 278$ mhos, as in Table VIII above, the concentration of potassium ion is calculated as $113/278 \times 1{\cdot}00\ \mathrm{N} = 0{\cdot}41\ \mathrm{N}$.

Now in Tables I and V the experimental result is that the sum total of all crystalloidal substances present in 1·00 N solutions such as K Str., $\mathrm{K}^{\cdot}$ and Str.′ is 0·42 normal. Of this, then, 0·41 has to be taken for the potassium ion $\mathrm{K}^{\cdot}$, leaving only 0·01 normal to include everything else. Instead of a total of 0·01 normal, at least 0·42 would have been required for the stearate ion if present, and a further 0·58 for the normal un-ionised material. Thus practically all of the negative ion must be in a colloidal form, in addition to the whole of the un-ionised material as well.

Apart from 0·41 N potassium ion, the whole of the stearate, including whatever carries the equivalent of this large amount of electricity, must be colloid and not simple unpolymerised stearate of any sort.

This evidence for the existence of the ionic micelle is not affected by varying the assumption with regard to the mobility of the carriers of the negative electricity within admissible limits. Thus, if we take the mobility as zero, ascribing all the conductivity to the potassium ion, the concentration of the latter would have to be 0·60 N; but the osmotic pressure is that of 0·42 N total crystalloid as a maximum, and this enormous amount of positive electricity has to be counterbalanced by an equal number of negative charges. If the negative carriers were credited with the same mobility as the acetate ion, 116 mhos, the concentration of potassium ion works out at 0·37 N, leaving only 0·07 N crystalloid to include 0·37 N stearate ion if present, in addition to any unpolymerised neutral soap. In Section X it will be shown that it is necessary to ascribe to the ionic micelle a mobility twice as great as that of the true stearate ion and equal to that of the potassium ion itself.

IX. *An Explanation of the Ionic Micelle on Mechanical Grounds.*

What is essentially new in the conception of a mobile micelle is the mechanism by which the micelle is built up round an aggregate of simple stearate ions which still retain their original electrical charges.

In the study of such electrolytic colloids as the proteins, it has long been assumed that an ion could be colloidal or associated with colloidal matter, but that was chiefly because quite enormous values are taken for the molecular weights of proteins, and molecules of such bulk must be expected to behave like colloids. Only a relatively low conductivity has ever been ascribed to them.*

The conception of these highly mobile, heavily hydrated micelles was originated by one of us in a 'General Discussion on Colloids and Viscosity,' held by the Faraday Society in 1913.† It was put forward to remove one of the chief difficulties in interpreting the properties of acid and alkali albumens, since it reconciles their enormous viscosity with their quite good conductivity.

Stokes's law applied to a sphere of radius a moving through a liquid of viscosity η may be expressed as follows:

$$V = \frac{F}{6\pi\eta a}$$

where V is the velocity caused by the action of a force F. Perrin and others have shown that this law applies to colloidal particles. In conductivity experiments, the force F is due to the electric charge on the ion, which is 96,540 coulombs per gram ion.

If this charge could be varied without other alteration of the ion, the driving force, velocity, and mobility or conductivity would vary in direct proportion.

If, on the other hand, a number of ions, say a dozen, were to coalesce, the resulting particles would be driven by a force equal to 12F. The velocity would not be proportionally great, for the radius of the sphere would now be increased by $a \times \sqrt[3]{12} = 2{\cdot}3a$. The new velocity would therefore be

$$\frac{12}{2{\cdot}3b} = 5{\cdot}2V.$$

This five-fold increase in mobility of the aggregate as compared with the separated ions would in practice be counterbalanced by the effect of the greatly enhanced electrostatic potential of the aggregate in attracting water molecules and other material, so that such an aggregate would become a heavily hydrated micelle. This great hydration would usually more than offset the extra mobility expected, and the result would be a colloidal particle of somewhat less mobility than a rather slow true ion. The hydration accounts for the enormous mechanical viscosity observed in all the systems mentioned and also for its variation with the concentration of the constituents, etc. Such hydration has for other reasons been commonly deduced by workers in this field.

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* It is a well-known and striking fact that many mechanical suspensions as well as colloidal particles have an actual mobility in the electrical field comparable with that of an ion. This has not, however, been associated with high conductance, for it has been generally explained on the Helmholtz conception of the shearing of an electrical double layer, water upon water, not on the assumption of such high electrical charge as we are here forced to recognise. Thus high mobility has not meant high conductivity, although both must be attributed to an ionic micelle.

† 'Trans. Faraday Soc.,' vol. 9, p. 99 (1913); 'Kolloid-Zeitschr.,' vol. 13, p. 56 (1913).

X. *The Constitution of Dilute Solutions of Soap.*

On account of the limitations of this method, N/5 soap solutions were the most dilute investigated. The result of measurements with 0·20 N potassium palmitate solution at 90° was as follows:—

Lowering of dew-point = rise of boiling-point at 90° = 0·12°.

Hence total concentrations of all ions and molecules present = 0·25 N.

Now the molar conductivity of N/5 potassium palmitate at 90° is 111·0 reciprocal ohms. If the conductivity at infinite dilution is 304, the concentration of potassium ions is 0·072 normal; if it be 278, the concentration is 0·080 normal K′.

Hydrolysis does not affect this result by more than about 2 per cent., which may be neglected for our present purpose.

Taking the second result, K = 0·080 N, total crystalloids present being 0·25 N, this leaves a concentration of 0·25 – 0·08 = 0·17 N crystalloids other than potassium ion. The total undissociated soap is 0·200 – 0·080 = 0·120 N. Thus, even if all the undissociated soap here is in simple crystalloidal form, there is still 0·17 – 0·12 = 0·05 normal crystalloid to account for, and this must be simple palmitate ions, since the hydroxyl ions have been shown to be only about 0·01 normal. The small balance of 0·03 is all that can be colloid.

Whether this relatively small amount of colloid is due to remaining micelle or to neutral colloid will be discussed below. The point to notice is that not more than a quarter of the undissociated palmitate, nor more than three-eighths of the palmitate ion may be in colloidal form. If there be some of each in colloidal form, this amount has to be divided up between them, so as not to exceed a total of 0·03 normal.

It is quite clear that in N/5 palmitate solution the breakdown of the colloid has gone moderately far, and that further dilution would rapidly complete it. In other words, we have a clear case of transition from colloid to crystalloid in the same solution, depending only on the concentration, and forming a true, stable, reversible equilibrium in each concentration. That a colloid can thus enter into true equilibria would appear to be of great importance for the theory of colloids.

XI. *The Mobility and Hydration of the Ionic Micelle.*

The results deduced in Tables V—XII are based upon a provisional assumption that the conductivity of the ionic micelle is equal to that of the fatty ions it has replaced.

However, the data in Tables IX—XII for 1·5 N solutions of potassium laurate, sodium stearate, and sodium palmitate show that the osmotic effect is less than that required upon this basis for the potassium or sodium ion alone. This cannot be due to the fact that uncorrected osmotic data always appear too high and conductivity data too low, as was pointed out in Section VII above, for this circumstance operates in the reverse direction from that required to explain the present data for these three solutions.

To reconcile the osmotic effect with the observed conductivity, it is therefore necessary to ascribe to the ionic micelle in these 1·5 N solutions a mobility at least twice as great as that of the true ion it has replaced. Thus, instead of a mobility of 90 mhos, the value in these concentrations must be about equal to that of the potassium ion, which is 188 mhos.

An alternative which we reject is the assumption of a positive as well as a negative micelle to replace some of the potassium ion. It is not in accordance with what we know of the behaviour of colloids that two oppositely charged colloids should be simultaneously present in the free condition. Experiments which were in progress in 1914, and are now being completed, afford direct measurements of the concentration of potassium and sodium ions present, and therefore remove any uncertainty upon this point.

Our conception is that the mobility of the ionic micelle increases with concentration. Important confirmation is given, for example, by the conductivity. It is definitely a fact that the higher soap solutions, quite apart from the small amount of free alkali present, exhibit minimum conductivity in tenth or fifth normal solutions. (Previous papers from this Laboratory, also confirmed by the experiments of F. Goldschmidt and co-workers.)* In higher concentrations the conductivity rises appreciably up to half normal or normal solutions, where a maximum is observed. This is direct evidence that the ionic micelle which is replacing the fatty acid ion is a better conductor than that ion. The ultimate falling off in very concentrated solutions is the effect of the diminishing dissociation of the electrolytic colloid.

The higher soaps are the most colloidal, and the potassium soaps contain more colloid than the sodium salts. It is just these cases that exhibit the minimum in decinormal solution. The better conducting and less colloidal potassium laurate (C_{12}), and the sodium soaps, do not show a minimum until fifth normal solution is attained.

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* Ubbelohde and Goldschmidt, 'Handbuch der Oele und Fette,' vol. 3, Leipzig (1910–11); 'Zeitschr. Electrochem.,' vol. 18, p. 380 (1912); 'Kolloid-Zeitschr.,' vol. 12, p. 18 (1913); 'Kolloid-Chem. Beihefte,' vol. 5, p. 427 (1914).

Again, the lowering of vapour pressure passes through a maximum in normal solution, where the total concentration of crystalloid is at a maximum. Diminishing hydration and diminishing dissociation of the colloidal electrolyte combine to reduce the lowering of vapour pressure, and it therefore falls to the minimum observed in one and a half normal solution. There must be a limit to this action, as the proportion of total water present gets less, hence the minimum at 1·5 normal.

Diminishing hydration with increasing concentration of the micelle, or some other alteration in the formula of the micelle, follows again from the principle of mass action, for otherwise within a very narrow range of concentration the colloidal electrolyte would pass completely into an undissociated form and no longer conduct.

The diminishing hydration is not due to water becoming scarce, for the fact that the vapour pressure of 1·5 N solution is greater than 1·0 N solution means that water is more available in the former than in the latter. The hydration being less in 1·5 N, where the water is most active and available, can only be explained by some such alteration in the formula or structure of the micelle as the increasing proportion of undissociated soap in it.

Other evidence in support of this assumption will be discussed below in Sections XII and XIV. Decrease of hydration with rise of temperature explains other conductivity data of the previous papers; this will be discussed in a separate communication.

Reverting to the consideration of Tables VIII–XI, these appear then to be substantially correct for all dilute solutions. For most solutions, they probably indicate minimum values for the amounts of colloid present. For the most concentrated solution of the higher soaps, the formation of colloid is necessarily less than that given in the Tables, but these solutions appear to contain little else than colloid, together with potassium or sodium ion.

XII. *The Formula of the Ionic Micelle.*

Various views may well be taken with regard to the formation of the ionic micelle. The simplest is to consider it as an agglomeration of palmitate ions, heavily weighted by water, a complex solvate:—

$$(P')_n \, . \, (H_2O)_m. \qquad (1)$$

The second and chief of the possible alternative formulæ, and that which appears to us most plausible, is that all or nearly all the colloid collects in the ionic micelle:—

$$(NaP)_x \, . \, (P')_n \, . \, (H_2O)_m. \qquad (2)$$

Other hypotheses, based upon assumption of extensive hydrolysis, compensated by nearly quantitative sorption of the hydroxyl ion, give identical composition, with a different structure. Such formulæ, however, have been excluded through direct measurements of the sorption of sodium hydroxide, which is found to be only very small; some of the data for this have already been published. Similarly, the existence of such a hydrogen soap as Reychler's cetyl sulphonic acid, in which hydrolysis is out of the question, renders such strained conceptions valueless.

That a water sphere should collect around these enormous electrical charges is as inevitable as the collection of a droplet of water round an electron in saturated water vapour; but, if the undissociated colloid also joins in, it leads to formula (2).

In formula (1) above, driving back the dissociation does not so much alter the composition of the ionic micelle, but, instead, replaces it by the neutral colloid produced. This hypothesis, that the micelle contains but little of the undissociated soap, which exists independently as a neutral colloid, can be made to account for the chief facts relating to soap solutions, although not so readily as formula (2). In dilute solutions, as was shown in previous sections, neutral undissociated soap does exist independently, but in simple crystalloidal form.

Formula (2) presents a general scheme for the composition of the micelle, which would alter continuously with concentration, or upon the addition of salts. Thus, in very concentrated solution, or in the presence of large amounts of another electrolyte, such as sodium hydroxide (see below), the soap must be nearly all colloid, of approximately the composition

$$x\text{NaP} \,.\, m\text{H}_2\text{O}. \tag{3}$$

This change of composition upon increasing the concentration would, as suggested in Section XI, serve to explain the surprisingly great mobility and diminished hydration of the micelle in concentrated solution, where the mobility is more than double that which would have been predicted from the properties of complex ions hitherto studied.

A further argument for the conception embodied in formula (2) is the divergence in behaviour between the potassium and sodium soaps. This cannot be so readily explained if the micelle in both is identical, as is required for formula (1). But, according to formula (2), it becomes quite possible that the sodium and potassium soap micelles should differ distinctly, as they do.

XIII. *Possible Limits of Concentration of Ionic Micelle Present.*

We have shown how the approximate values of the concentrations of the total crystalloid and total colloid can be arrived at. We have now to attempt to allocate the total colloid between neutral colloid and micelle and the total crystalloid between undissociated soap, sodium or potassium ion, and simple fatty ion. This is at present possible only within the definite limits set out in the Tables below.

For the purpose of the present section, the distinction will be drawn as between the agglomerated palmitate ions in the ionic micelle and the remainder of the colloid, termed neutral colloid. It is clear that the numbers retain their full significance, whether formula (1) above, or the more probable formula (2), is accepted, where part or most of the neutral colloid is taken up by the ionic micelle

$$(P')_n \,.\, (H_2O)_m \,.\, (NaP)_x. \tag{2}$$

The data given represent in both cases the amount of soap present as $(P')_n$ in the ionic micelles. The concentrations of "neutral colloid" set out in the Tables include the soap present as $(NaP)_x$ in the ionic micelles.

The results, which are recorded in Tables XIII–XVI, are based upon the two extreme possibilities. The first figure of each pair allocates the total colloid as far as possible to ionic micelle; this cannot, of course, exceed the concentration of potassium or sodium ions, and any excess above this must necessarily be ascribed to neutral colloid. This procedure fixed the minimum possible values for simple fatty acid ion P′, and also the maximum possible amount of simple undissociated soap, NaP.

The second figure in each case gives the opposite extreme consistent with our measurements, allotting the total colloid to neutral colloid as far as possible; the maximum limit to the neutral colloid here is the total amount of undissociated soap obtained by subtracting the concentration of potassium or sodium ions from the total concentration of the solution; any excess of colloid must be recognised as ionic micelle.

Table XII.—Limits of Concentration of Colloidal Constituents of K Salts.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate, C_{10}.	Caprylate, C_8.	Caproate, C_6.
Agglomerated Ions in the Ionic Micelle.							
0 ·2 N	0 ·06–0 ·00	0 ·03–0 ·00	0 ·02–0 ·00	0	0	0	0
0 ·5 N	0 ·21–0 ·06	0 ·20–0 ·01	0 ·24–0 ·01	0 ·22–0 ·00	0 ·14–0 ·00	0 ·06–0 ·00	0 ·02–0 ·00
0 ·75 N	0 ·31–0 ·23	0 ·35–0 ·24	0 ·37–0 ·18	0 ·38–0 ·14	0 ·28–0 ·00	0 ·17–0 ·00	0 ·08–0 ·00
1 ·0 N	0 ·41–0 ·40	0 ·45–0 ·40	0 ·49–0 ·40	0 ·52–0 ·37	0 ·44–0 ·00	0 ·28–0 ·00	0 ·15–0 ·00
1 ·5 N	—	—	—	0 ·70–0 ·75			
2 ·0 N	—	—	—	0 ·89–0 ·78	—	0 ·90–0 ·16	
"Neutral Colloid."							
0 ·2 N	0 ·00–0 ·06	0 ·00–0 ·03	0 ·00–0 ·02	0 ·00	0 ·00	0 ·00	0 ·00
0 ·5 N	0 ·14–0 ·29	0 ·11–0 ·30	0 ·03–0 ·26	0 ·00–0 ·22	0 ·00–0 ·14	0 ·00–0 ·07	0 ·00–0 ·02
0 ·75 N	0 ·38–0 ·46	0 ·29–0 ·40	0 ·19–0 ·38	0 ·13–0 ·37	0 ·00–0 ·28	0 00–0 ·17	0 ·00–0 ·08
1 ·0 N	0 ·58–0 ·59	0 ·50–0 ·55	0 ·42–0 ·51	0 ·33–0 ·48	0 ·00–0 ·44	0 ·00–0 ·28	0 ·00–0 ·15
1 ·5 N	—	—	—	0 ·85–0 ·80			
2 ·0 N	—	—	—	1 ·00–1 ·11	—	0 ·36–1 ·10	

Table XIII.—Limits of Concentration of Crystalloidal Constituents of K Salts at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Caprate, C_{10}.	Caprylate, C_8.	Caproate, C_6.	Acetate, C_2.
Simple Fatty Acid Ion.								
0 ·2 N	0 ·01–0 ·07	0 ·05–0 ·08	0 ·07–0 ·09	0 ·11–0 ·10	0 ·14–0 ·14	0 ·15–0 ·14	0 ·15–0 ·14	0 ·19–0 ·15
0 ·5 N	0 ·00–0 ·15	0 ·00–0 ·19	0 ·00–0 ·23	0 ·04–0 ·26	0 ·14–0 ·28	0 ·23–0 ·30	0 ·29–0 ·31	0 ·45–0 ·32
0 ·75 N	0 ·00–0 ·08	0 ·00–0 ·11	0 ·00–0 ·19	0 ·00–0 ·24	0 ·12–0 ·40	0 ·22–0 ·39	0 ·35–0 ·43	0 –0 ·45
1 ·0 N	0 ·00–0 ·01	0 ·00–0 ·05	0 ·00–0 ·09	0 ·00–0 ·15	0 ·08–0 ·52	0 ·25–0 ·53	0 ·37–0 ·52	0 ·78–0 ·58
1 ·5 N	—	—	—	0 ·00–0 ·05	—	—	—	0 –0 ·80
2 ·0 N	—	—	—	0 ·00–0 ·11	—	0 ·00–0 ·74	—	0 –1 ·01
Simple Neutral Undissociated Salt.								
0 ·2 N	0 ·13–0 ·07	0 ·12–0 ·09	0 ·11–0 ·09	0 ·10–0 ·11	0 ·06–0 ·06	0 ·07–0 ·08	0 ·06–0 ·07	0 ·01–0 ·05
0 ·5 N	0 ·15–0 ·00	0 ·19–0 ·00	0 ·23–0 ·00	0 ·24–0 ·02	0 ·22–0 ·08	0 ·20–0 ·13	0 ·19–0 ·17	0 ·05–0 ·18
0 ·75 N	0 ·08–0 ·00	0 ·11–0 ·00	0 ·19–0 ·00	0 ·24–0 ·00	0 ·38–0 ·07	0 ·36–0 ·19	0 ·32–0 ·24	0 –0 ·30
1 ·0 N	0 ·01–0 ·00	0 ·05–0 ·00	0 ·09–0 ·00	0 ·15–0 ·00	0 ·48–0 ·04	0 ·47–0 ·19	0 ·48–0 ·33	0 ·22–0 ·42
1 ·5 N	—	—	—	–0 ·05–0 ·00	—	—	—	0 –0 ·75
2 ·0 N	—	—	—	0 ·11–0 ·00	—	0 ·74–0 ·00	--	0 –0 ·99

Table XIV.—Limits of Concentration of Colloidal Constituents of Na Salts at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Acetate, C_2.
Agglomerated Ions in the Ionic Micelle.					
0·2 N	0·02–0·00	0·01–0·00	0·00–0·00	−0·03–0·00	0·00–0·00
0·5 N	0·17–0·00	0·20–0·00	0·22–0·00	0·16–0·00	−0·03–0·00
0·75 N	0·27–0·09	0·29–0·08	0·32–0·06	0·35–0·04	0·00–0·00
1·0 N	0·39–0·30	0·37–0·22	0·41–0·21	0·46–0·21	−0·23–0·00
1·5 N	0·53–0·73	0·55–0·66	0·54–0·52	0·62–0·55	0·00–0·00
"Neutral Colloid."					
0·2 N	0·00–0·02	0·00–0·01	0·00–0·00	0·00–0·00	0·00–0·00
0·5 N	0·13–0·30	0·08–0·28	0·00–0·22	0·00–0·16	0·00–0·13
0·75 N	0·30–0·48	0·25–0·46	0·17–0·43	0·09–0·40	0·00–0·00
1·0 N	0·52–0·61	0·48–0·63	0·39–0·59	0·29–0·54	0·00–0·23
1·5 N	0·17–0·97	1·06–0·95	0·94–0·96	0·81–0·88	0·00–0·00

Table XV.—Limits of Concentration of Crystalloidal Constituents of Na Salts at 90°.

Weight normality.	Stearate, C_{18}.	Palmitate, C_{16}.	Myristate, C_{14}.	Laurate, C_{12}.	Acetate, C_2.
Simple Fatty Acid Ion.					
0·2 N	0·03– 0·05	0·07– 0·08	0·09–0·09	0·13–0·10	0·00–0·00
0·5 N	0·00– 0·17	0·00– 0·20	0·00–0·22	0·08–0·24	0·43–0·30
0·75 N	0·00– 0·18	0·00– 0·21	0·00–0·26	0·00–0·31	0·00–0·00
1·0 N	0·00– 0·09	0·00– 0·15	0·00–0·20	0·00–0·25	0·74–0·51
1·5 N	0·00––0·20	0·00––0·11	0·00–0·02	0·00–0·07	0·00–0·00
Simple Neutral Undissociated Salt.					
0·2 N	0·15– 0·13	0·12– 0·11	0·11–0·11	0·10–0·13	0·06–0·06
0·5 N	0·20– 0·03	0·22– 0·02	0·28–0·06	0·26–0·10	0·20–0·33
0·75 N	0·18– 0·00	0·21– 0·00	0·26–0·00	0·31–0·00	0·34–0·34
1·0 N	0·09– 0·00	0·15– 0·00	0·20–0·00	0·25–0·00	0·49–0·72
1·5 N	−0·20– 0·00	−0·11– 0·00	0·02–0·00	0·17–0·10	0·84–0·84